


The formaldehyde challenge

Developments on next generation latex binders





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HOFER VLIESSTOFFTAGE

Content

Synthomer - Top 5 global supplier of emulsion polymers

Technical solution provider & broadest chemistry offering & strengthened positon in the US

Divisions & Markets

EMEA Division | **ASIA Division** | **AMERICAS Division**

- Construction & Coatings
- Adhesives & Sealants
- Textile & Fibre Bonding
- Carpet & Foam
- Paper
- Health & Protection

SPECIALITIES Division

- Performance Polymers
- Compounds
- William Blythe (inorganic specialities)
- Powder Coatings
- Monomers

USD 1.32 bn
Group revenue

26
Production sites

2700
Employees

> 100
Counties

- Annual sales volume of Synthetic Latex : 1.56 Mio MT
- Broadest Latex offering -> XSBR, XNBR, SA, PA, VA, VACo, VP, ABS, CR, NR*

*: pre-vulcanized

Let us face the Formaldehyde (FA) Challenge – the general view

Key raw material with significant Health and Safety implications

Some FA key facts

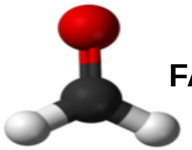
- naturally occurring compound
- colorless gas with pungent odor
- density: 0,815 g/ cm^3
- vapor pressure: 0,43 – 044 MPa
- high water solubility

- estimated production 8,7 Mio t per year [(1)]
- precursor for industrial resins (urea, melamine, phenol etc.)
- exemplary resin applications: plywood, coatings, textiles (as finishing component)

- classification: Toxic (T), corrosive (C) carcinogen cat 1B, H 350

Health and Safety Implications for the Textile industry

- multiple regulations on end articles and product labels
- workplace: standards on MAC levels, emission levels, air quality control requirements…
- limitation of FA emissions to lowest possible level by process - & technical measures
- regular check on substitution potential



FA

What can be done by the Latex supplier…

- no use of FA in raw material formulations ✓
- ban of FA emitting biocides ✓
- *development and implementation of new options for product cross-linking (-> resin substitution)*

[1)] Wiley-VCH, Ullmann´s Encyclopedia of Industrial Chemistry

Let us face the FA Challenge – the regulations view

Reclassification to carcinogen category 1 B as strong driver of regulation change

Reclassification in January 2016

Old
carcinogen category 2 B
H 351

New
carcinogen category 1 B
H 350

Effects on current limits

MAC values *
0,3 ml / m^3 (0,3 ppm)
0,6 ml / m^3 (0,6 ppm)

TRGS 900*
0,3 ml / m^3 (0,3 ppm)

carcinogen category 1
mutagen category 2

regulated by carcinogen EU Directive in EU workplaces

exposure should be as low as technically possible using hierarchy of preventions

MAC values

- No new limits set yet
- WHO recommendation 0,08 ml/m^3

Emmission values

- No new limits set yet – current TA Luft: 20 mg /m^3
- LAI recommendation 5 mg / m^3 or 12,5 g/h (Feb 2020)

*: Germany, individual regulation per country

Cross-linking – high performance by polymer networks

Key for may high performance Latices – chemical bonding & finishes

Concept of cross-linking

Creation of **chemical bonds** leading to an increase of the molecular weight and the formation of **polymer networks**

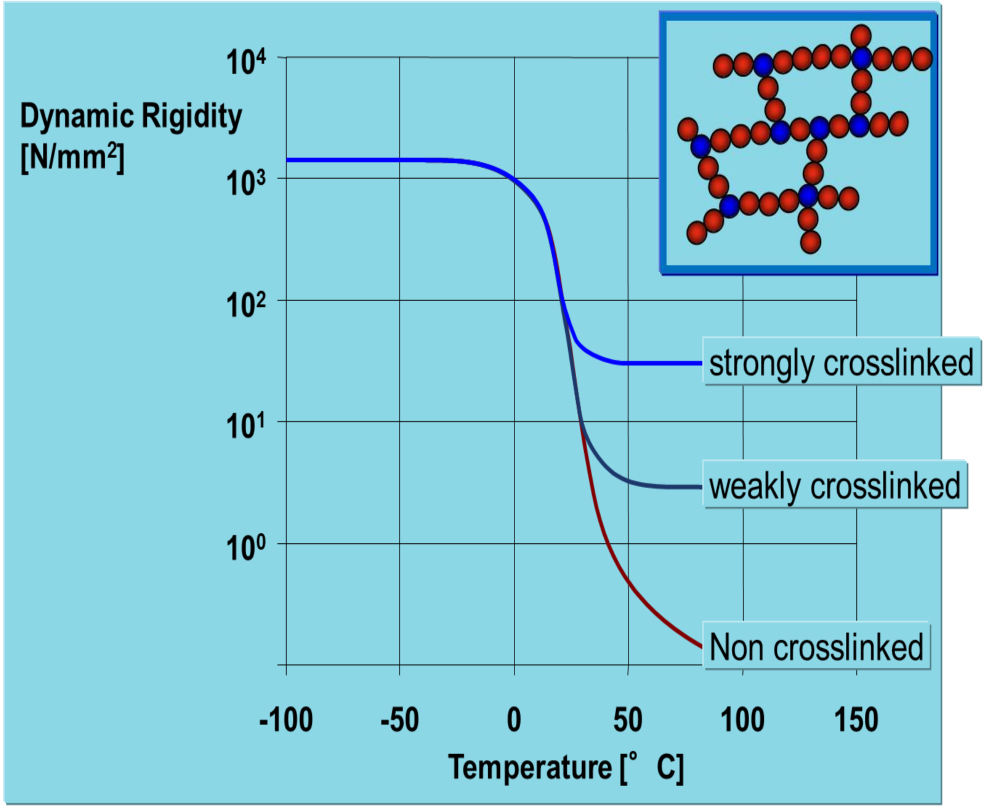
A) Cross-linking during the polymer synthesis
-> monomers with 2 or more double bonds
-> process conditions
B) Cross-linking during the polymer film drying
-> by functional group within the polymer backbone
-> more sophisticated than A
Allows ideal wetting and bonding to the fiber substrate

Cross-linking leads to high performance on:

- elasticity and resilience
- heat resistance
- tensile - / bonding strength
- resistance against solvents, acids, chemicals
- combination of soft handle & none blocking features
- better abrasion resistance
- improved wrinkle behavior

Cross-linking

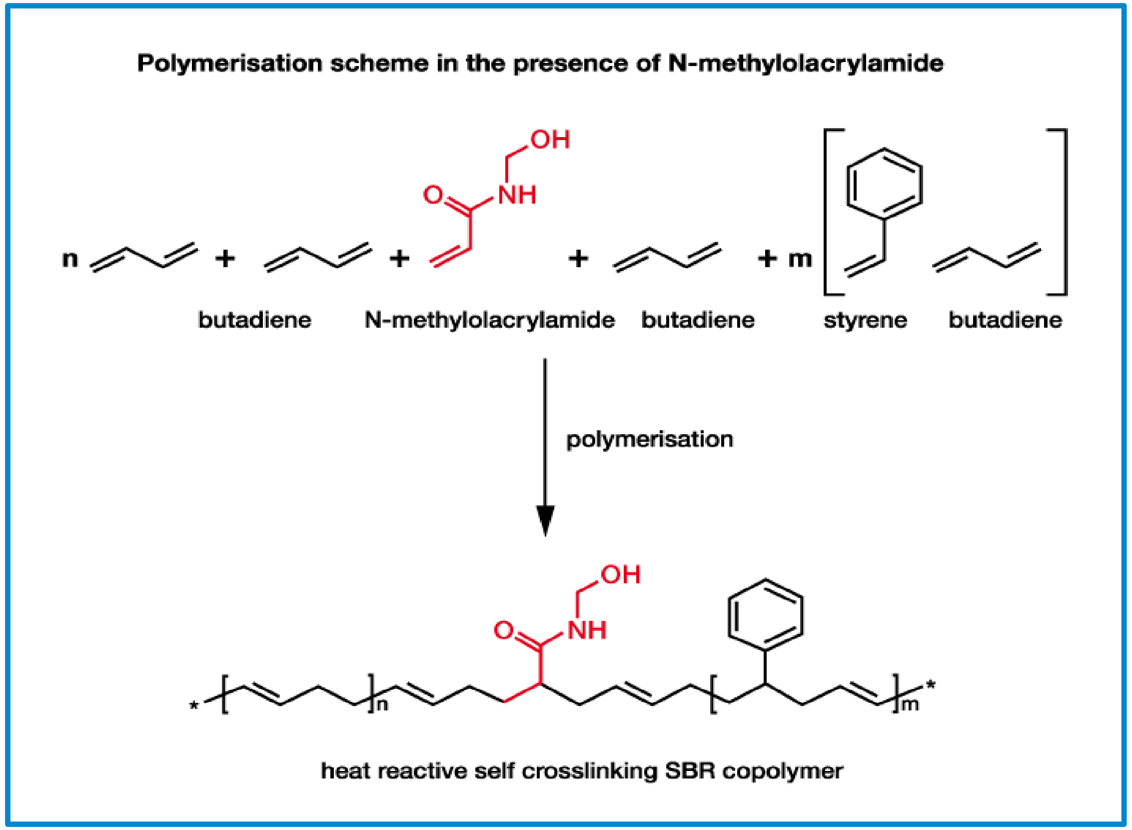
Impact on elasticity and resilience by

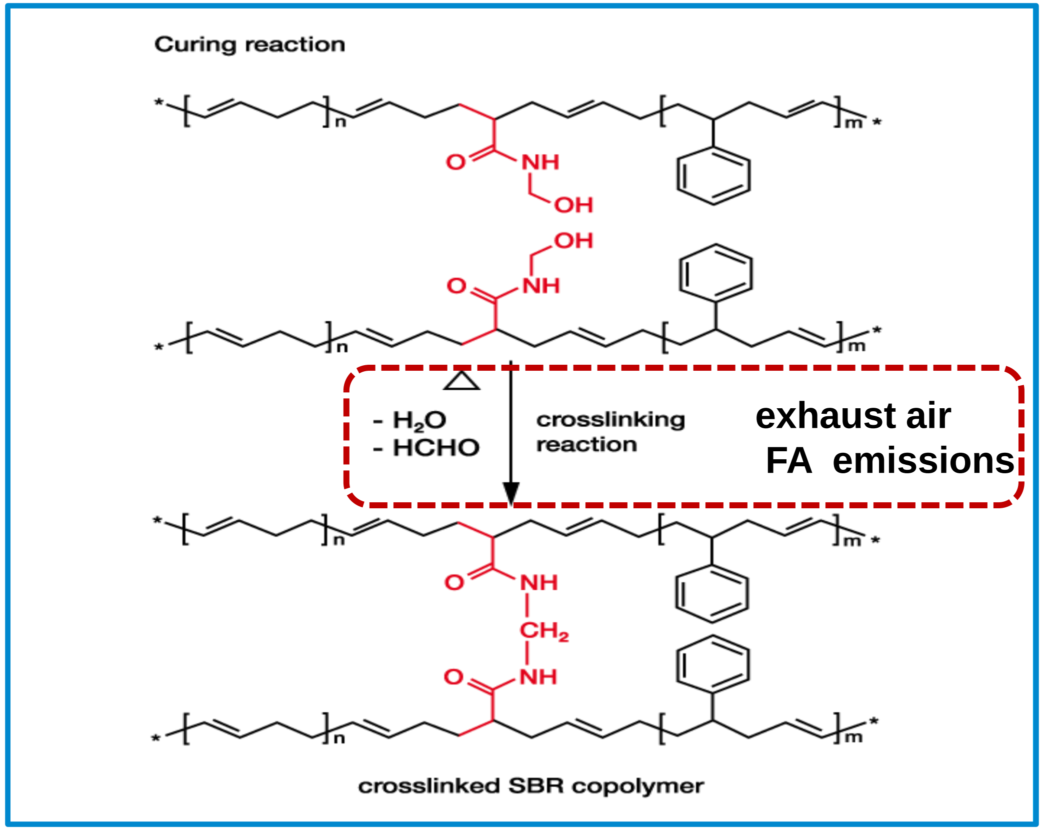


Cross-linking during film formation as preferred approach

State of the art technology… but FA emissions in ppm range

Cross-linking technology with N-methylolacrylamide





- special heat reactive co-monomers are included in the polymer chain during polymerization
- reaction at 130° C in the dry state after film formation

FA Analytics (1) - A method overview for finished Textiles

The method matters – focus on free and hydrolysable FA

Analysis of Textile samples

- analysis of water extract
- photometric identification via colored reaction products
- detection of free and hydrolyzable FA
- significant differences on
- -> sample size
- -> extraction conditions (temp., time, mixing)
- -> hydrolysis level
- hydrolysis level depending on temp. and pH
- single detection of free FA requires high pH and low temperature [1]

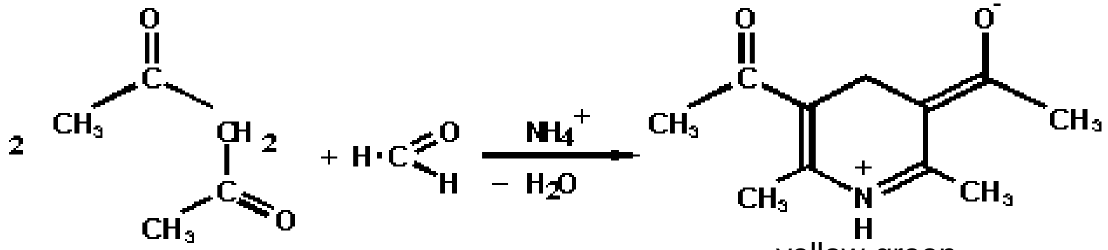
Some textile test standards

USA: AATCC Test
Japan: MITI – JIS Law 1041, Law 112
UK: Shirley I ("free") , Shirley II ("released")
D: DIN ISO 14184-1

[1] Method of de Jong and de Jonge

Photometric FA identification

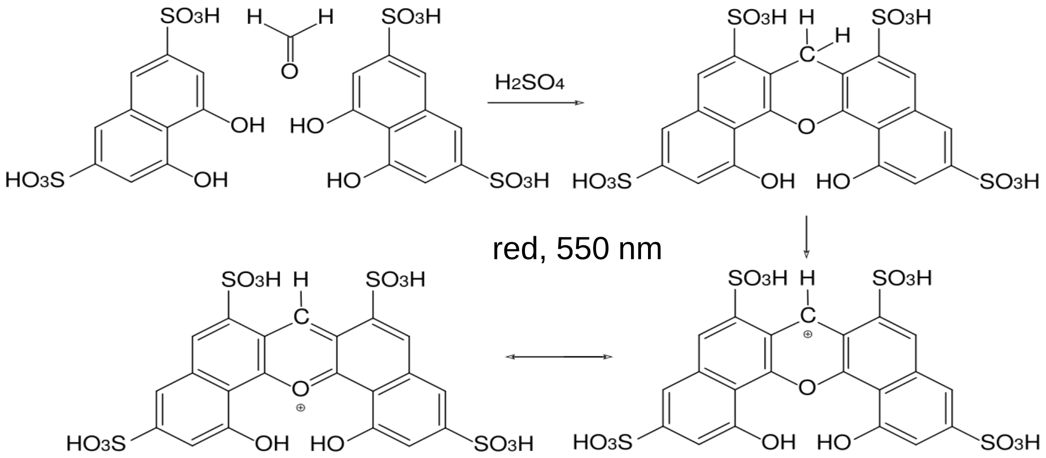
A) Acetylacetone reaction NASH reaction



yellow-green

412nm.

B) Chromotropic acid in H_2SO_4 solution



FA Analytics (2) - A method overview for finished Textiles

A detailed look into the most common tests used for Textiles

Method	MITI Law 1041	Japan Law 112	AATCC 112-82	Shirley I "free"	Shirley II "released"	DIN ISO 14184-1
Extraction conditions	1g 100 ml water 1h, 25 ° C wetting agent	1g 100 ml water 1h, 40° C	1g 50 ml water 20 h, 49° C sample cage	2g 20 ml water 20min, 25° C	2g 20 ml water 20 h, 49° C	1 g (2,5g) 100 ml water 1 h, 40° C
FA detection	Phloroglucin photometric	Acetylaceton photometric	Phloroglucin photometric	Chromotropic acid photometric	Chromotropic acid photometric	Acetylaceton photometric

hydrolysis level will increase with extraction time and temperature

Shirley I < MITI < Law 112
LAW 112 ~ DIN ISO < AATCC
AATCC ~ Shirley II

Other standards

- **Chinese Standard** T -18585-2008 most demanding due to steam distillation -> 2,5 g sample (textile *or Latex*), steam distillation to 250 ml volume, Acetylaceton
- **Total FA content** VDL RL03 (paint industry) steam distillation at low pH -> 10 g sample (sample *or Latex*) , 50 ml water, 20 ml 20%ige H_2SO_4, Acetylaceton

FA Analytics (3) - FA release at processing

TEGEWA method as reference point for FA emissions / FA exhaust emissions by VDI 3862

TEGEWA Method

FA emissions at processing of aqueous based systems

- 1g liquid sample evenly dispersed over 3 g of sand
- heating for 5 min at 160 ° C
- emissions are carried over to 2 water filters with 50 and 25 ml water using a nitrogen flow of 200ml/min
- IR heating to prevent condensation in the tube connections
- FA analytics via Acetylaceton method in the collected water made up to 250 ml volume

VDI 3862 (part 6)

Determination of FA in exhaust gases

- 2 water filters (collectors) with 30 ml each
- exhaust gas flow rate 1 L / min (pump system) for 30 min
- typically 30 min measurement time
- heated sampling probe and dust filter (prevent condensation)
- FA analytic via Acetylaceton method
- recording of sample volume, time, temperature,
- cross sensitivities at higher levels of NH_3 and with $S0_2$

TEGEWA test set up

Case Study: PES roofing Felts

Cross-linking as key for flexible & strong & high temperature resistant PES roofing felts

Application

- PES for bituminous roofing felts

Manufacturing process

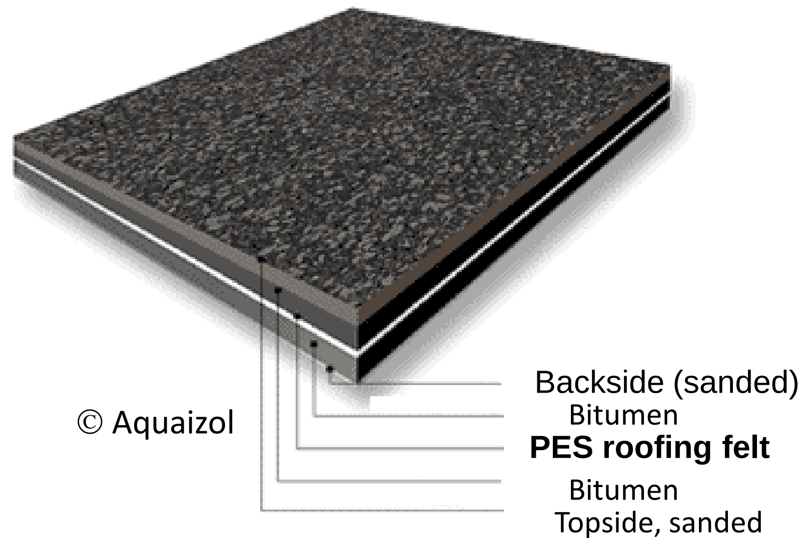
- staple fiber or spun bond non woven
- foulard impregnation, foam or liquor
- addition of up to 20 % formaldehyde resins as formulation additive
  -> 2 K system with limited pot life (main FA source)

Product requirements

- water resistance - > max reduction of tensile strength of 5%
- high tensile strength -> min. 700 N all 3 key dimensions
- high stiff handle but no kink or crack at flex test
- broad compatibility with thermo-set resins
- high aging stability and filler compatibility
- thermo- dimension stability at 200° C

Current state of the art product offering

- self cross-linking XSBR Latex (FA emissions in ppm range)
- Tg: 35° C, PS: 130 nm, TS: 50%, Viscosity: < 500 mPAs

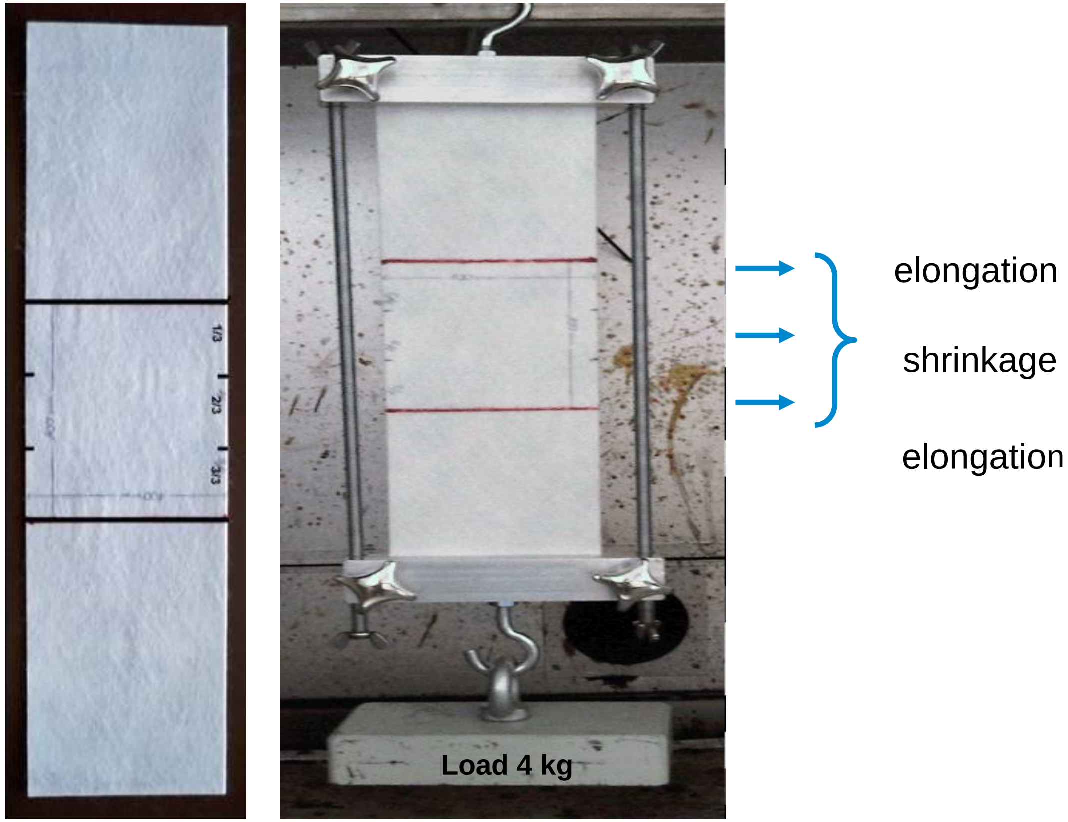


Targets

- 1 K system, no use of thermo- set resin
  -> reduced complexity
  -> no pot life limitations
- Cross-linking without FA emissions

Case study: PES roofing felts

Thermo- dimension stability as most demanding product feature, DIN 18192



3 samples, 100 mm x 360 mm
10 min 200° C, 5 min conditioning at RT

Targets

- dimensional elongation MD max 1,5 %
- dimensional shrink CD max 1,5 %
- test series: 4 kg load

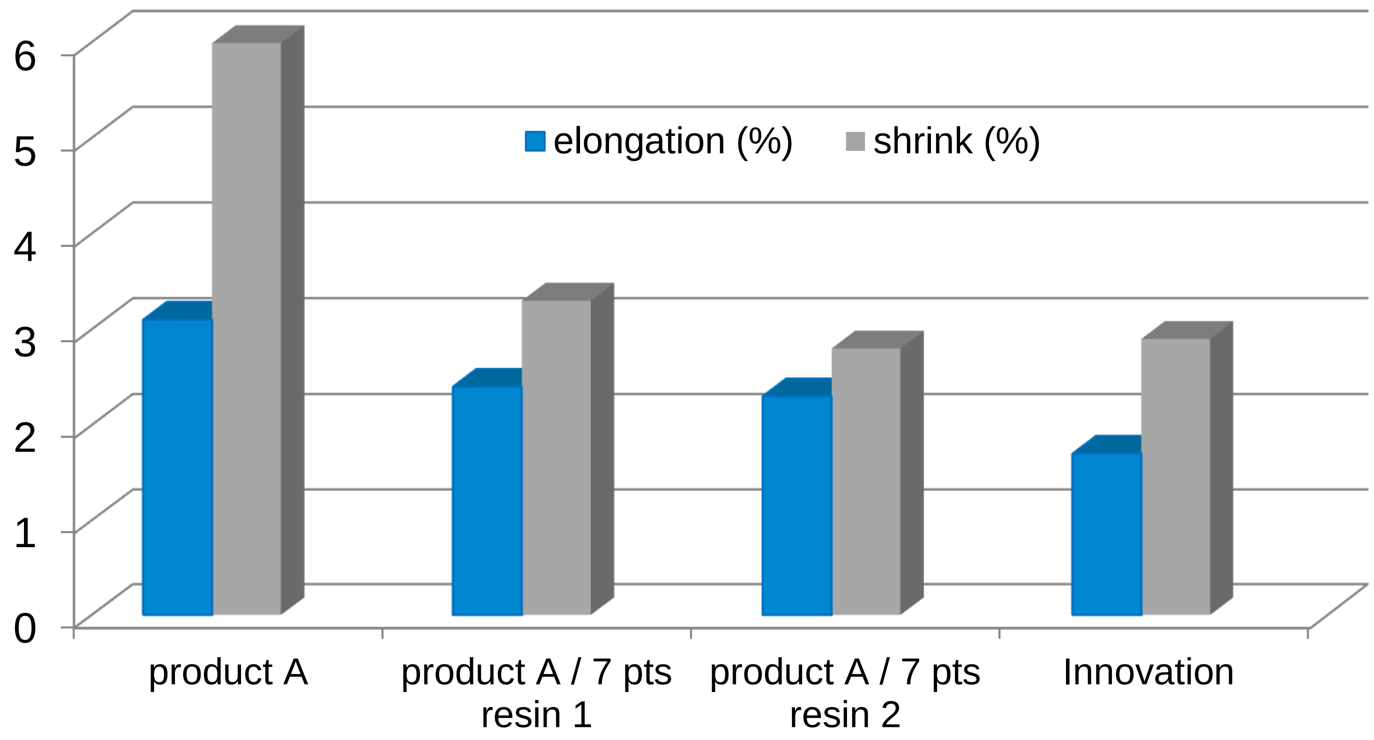
additional tests (not part of DIN)

- 8 kg load (target max 3 % elongation / 3% shrink)
- force needed for 5 %, 10% and 15 % elongation
- hot tensile strength (180 ° C)

Case study: PES roofing felts – FA free-cross-linking is feasible (1)

Strong performance on thermo-dimension stability

Thermo-dimension stability @ 200° C, 8 kg load



- PES non woven, 160 g/sqm,
- 20% coating weight d/d
- product A: market reference, **FA releasing**
- resins: MF resins, **FA releasing**
- Innovation: NEW **FA free** cross-linking XSBR

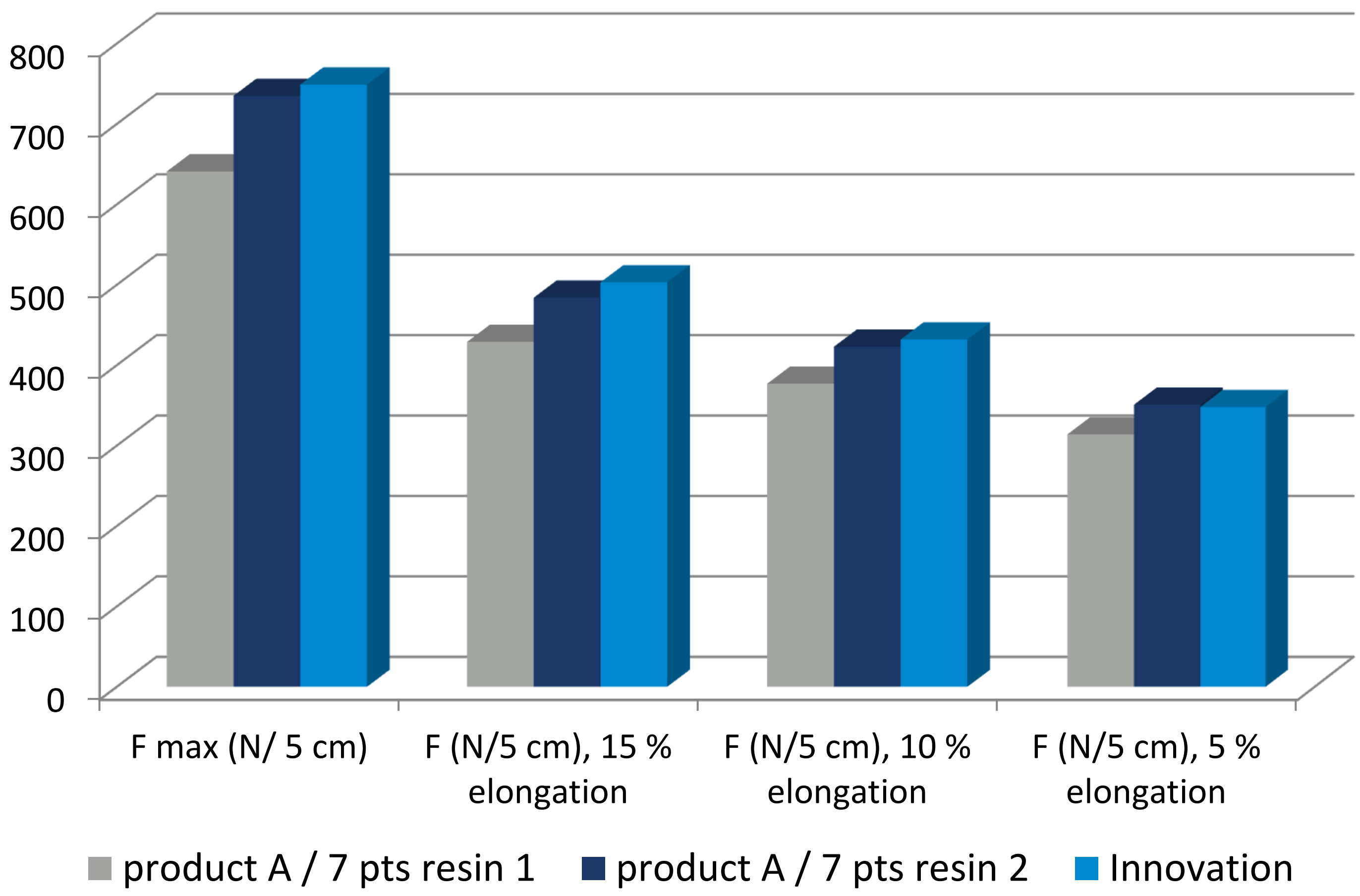
Results

- high performance on 200° C thermo- dimension stability fulfilled by Innovation product
- no extra MF resin needed
- 1 K solution feasible

Case study: PES roofing felts – FA free cross-linking is feasible (2)

New FA free crosslinking innovation with strong performance on tensile strength

Tensile strength, RT, MD, DIN 18192



- PES non woven, 160 g/sqm,
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- product A: market reference, **FA releasing**
- resins: MF resins, **FA releasing**
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Results

- high performance on tensile strength fulfilled by Innovation product
- no extra MF resin needed
- 1 K solution feasible

Summary & Outlook – Synthomer´s green Technology

Ultra low FA measurements results – Below detection limits of Law 112 and VDI 3862

FA Analytics

Market reference - self cross-linking

- Latex sample, Free FA (similar to Shirley I) : 100 – 200 ppm
- Latex sample, TEGEWA: several hundred ppm

Innovation products – FA free self cross-linking

- Latex samples
  free FA similar to Shirley I: < 10 ppm, at detection limit
  total FA according to VDL R03: < 10 ppm, at detection limit
- FA exhaust emissions
  VDI 3862 (part 6) < 0,16 ppm - below detection limit
- Textile samples
  according to Japanese Law 112 – below detection limit (5 ppm)

New FA free self cross -lining XSBR Latex

- high performance features based on FA free cross-linking
- no extra requirements on process conditions regarding coating / impregnation, line speed or drying conditions

Summary & Outlook – Synthomer´s green technology

How the FA challenge may open new opportunities to the Latex Industry…

New Opportunities by FA free cross-linking

Case Study: PES roofing felts

- 1 K product solution looks now feasible
  -> reduction of complexity
  -> no handling of extra thermo-set resins
  -> no process limitation by pot life

- Lower cross linking temperatures possible
  -> energy saving ?
  -> higher line output ?

Our commitment to environmentally preferred solutions translates into :
FA free cross- linking, APEO free, low VOC, material efficiency, renewable resources

Several other projects for FA free cross-linking

- PA -> sun blinds, block out curtains
- SA -> PRIPs, Deco Laminates
- XSBR -> alkali resistant glass mesh (EIFS)
- …




The formaldehyde challenge …

Thank you for your attention !

Questions ?